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Note

Reactive Deposition of W-, Mo- and V-doped SnO_2 Films

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Tin oxide films are well known as n-type semiconductors with excellent light transparency. The electro-conductive nature of the film is due to oxygen vacancies contained in the film. The investigations on the reactive deposition of the SnO_2 films have been made for the application of transparent electrodes. The undoped films exhibit relatively high resistivity of above 10^{-2} Ωcm.[1,2,3,4] Doping of Sb atoms in the films reduces the resistivity to the order of 10^{-3} Ωcm without alternating light transparency[5]. The authors further prepared W-, V- or Mo-doped films by the reactive evaporation method with great success. This note describes the effect of W, Mo and V dopants on the structure and physical properties of films.

Films were deposited in the conventional high-vacuum chamber evacuated by an oil-diffusion pump. The substrates were placed about 20 cm from the evaporation sources. Before deposition of films, the vacuum chamber was evacuated below 6.7×10^{-4}Pa. Tin was evaporated from an alumina crucible, and WO_3, MoO_3 and VO_2 were from a platinum crucible. Both Sn metal and the doping material were simultaneously evaporated with various ratios of evaporation rates. The deposition conditions were as follows : oxygen pressure, 0.67Pa; deposition rate, 1.5Å/sec; substrate temperature, 420°C. Films were deposited about 2700Å thick onto quartz glasses. The deposition rate and the film thickness were monitored by the quartz crystal oscillator which was calibrated to measure the film thickness at the substrates. The nominal concentrations of W in films were (0–20)mol%, and those of V and Mo were (0–10)mol%.

The dopant concentrations for several films were measured by EPMA analysis. The structure of films was examined by X-ray diffraction using Cu K_α radiation. Measurements of the electrical resistivity and the Hall coefficient for films were made by the Van der-Paw method. Light transmission of films was measured using a double-beam spectrophotometer.

Table 1 shows the concentrations of dopants in films determined by EPMA analysis together with those calculated from the evaporation rates of Sn metal and a dopant. The calculated values were in good agreement with the measured values within the experimental error, $\pm$0.4mol%.

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Table 1 Dopant concentrations in films (mol%)

kind of dopant	calculated	measured
W	2.1	1.7
W	4.8	4.7
W	13.0	12.6
V	4.2	3.9
V	9.0	9.5
Mo	2.0	2.2
Mo	5.9	6.2

This indicates that the concentrations of the dopants can be determined from the evaporation rates of Sn metal and a dopant.

Figure 1 shows X-ray diffraction patterns for typical films. All the films with the dopant concentrations below 10mol% exhibited good crystallinity with the rutil-like structure. Beyond this concentration, the crystallinity of films was deteriorated to some extent, which was indicated by the broadening of diffraction lines for the films. The lattice constants, a and c, were insensitive to kinds of the dopants and their concentrations. The values were in good agreement with the ASTM data (5–467; a=4.738Å, c=3.188Å) within the experimental error, ±0.005Å. However, the intensities of the diffraction lines of films were much deviated from those of the ASTM data, indicating the preferred orientation of films. The films doped with W or V above 1mol% exhibited a preferred orientation with a (110) plane parallel to the substrates, while the Mo-doped films

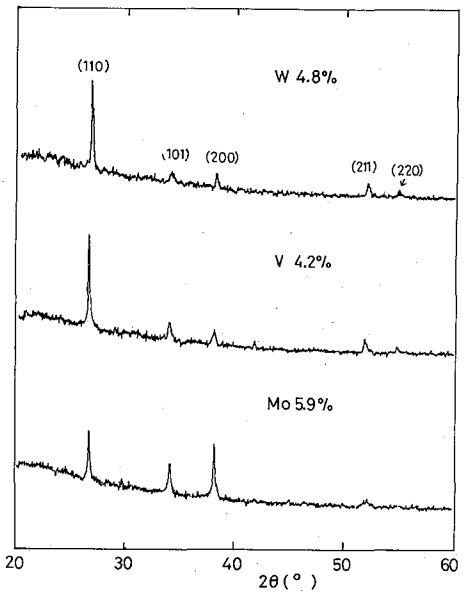

Fig. 1. X-ray diffraction patterns for films doped with 4.8mol%W, 4.2mol%V and and 5.9mol%Mo.

a preferred orientation with a (200) plane to some extent.

Figure 2 shows the dependences of the electrical resistivity, carrier mobility and carrier density of films on the W concentration. The results were very similar to those for the Sb-doped films.[5] The resistivity of the films was initially decreased with an increase in the W concentration up to about 2mol%. This is due to an increase in the carrier density. Tungsten atoms incorporated in the lattice are assumed to take a W^{5+} state and to liberate conduction electrons. As the W concentration increased above 2mol%, the resistivity of films increased rather steeply. The films doped with about 20mol%W exhibited much high resistivity, about 40 Ωcm. The increase in the resistivity at the higher W concentration is mainly attributed to a decrease in the carrier mobility. Tungusten atoms doped over 2mol% act only as the scattering centers for the carriers, resulting in a decrease in the carrier mobility. Beyond about 10mol%, the carrier mobility will be further reduced by the partial disorder of the lattice as indicated by the X-ray diffraction analysis, and this is responsible for the much high resistivity. Thus, the optimum doping level for the highest conductivity of films was about 2mol%W.

Figure 3 shows the dependence of the electrical resistivity on the V or Mo concentration. The V-doped films exhibited quite similar results to that of the In-dopped films.[5] The resistivity of V-doped films drastically increased with an increase in the V concentration. This increase was due to a decrease in the carrier density, because the carrier density was decreased to about $1.3 \times 10^{18}/cm^3$ as the V concentration increased to about 0.4mol%, while the carrier mobility was

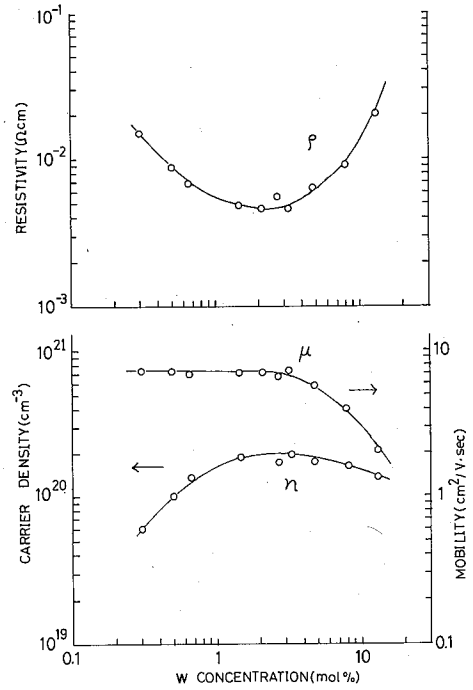

Fig. 2. Dependence of the electrical properties on the W concentration : ρ, resistivity; n, carrier density; μ, carrier mobility.

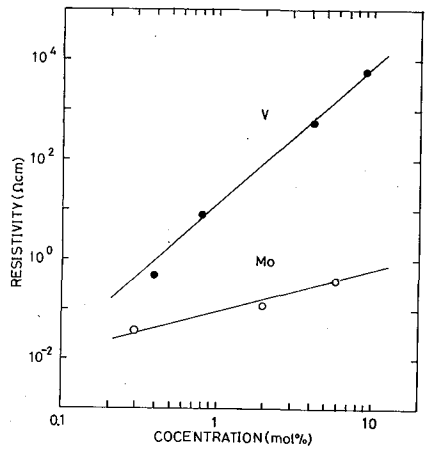

Fig. 3. Dependence of the resistivity on the V or Mo concentration.

almost unchanged taking the value of about 7 $cm^2/V \cdot sec$. The addition of V atoms to the lattice is assumed to reduce the number of oxygen vacancies, resulting in a decrease in the carier density at the higher V concentration.

The Mo-doped films exhibited a slight increase in the resistivity with increasing Mo concentration. The slight increase in the resistivity was similarly due to a decrease in the carrier density. For example, the values of the carrier density and the carrier mobility for the films with 2mol%Mo were $9.1 \times 10^{18}/cm^3$ and 6.8 $cm^2/V \cdot cm$, respectively. Doping of Mo atoms in the lattice will partly decrease the number of oxygen vacancies in films, which is responsible for the slight decrease in the carrier density at the higher Mo concentration.

Figure 4 shows light transmission curves for the W-doped films. The films doped with below about 3mol%W exhibited the high transmission of above 90%. Beyond about 3mol%, the

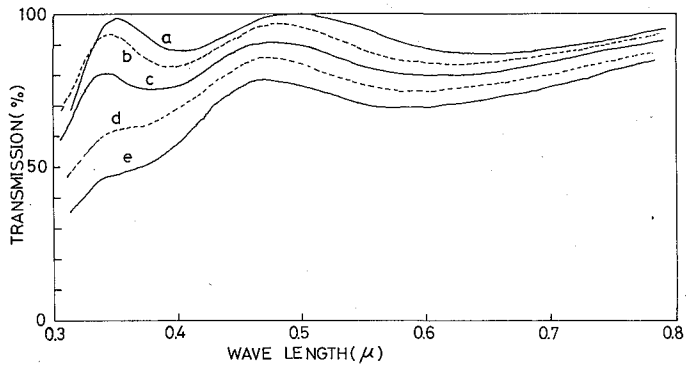

Fig. 4. Optical transmission spectra of films with various W concentrations : (a) 0mol%; (b) 2.7mol%; (c) 8.1mol%; (d) 13.0mol%; (e) 20.0mol%.

transmission of films was below 90%, and was gradually decreased with increasing W concentration. Both V- and Mo-doped films exhibited the high transmission of above 90% up to the concentration of about 10mol%.

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